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COMPLETE SPECIFICATION

Improvements in Laminates

We, THE DOW CHEMICAL COMPANY, a corporation organized and existing under the laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention pertains to a method of making new and useful film or foil structures of a layer of polyethylene or the like aliphatic hydrocarbon olefin polymer that is effectively and efficiently laminated or bonded to and supported upon a pre-formed substrate layer or sheet of "paper", and to the laminate structures produced by the method of this invention.

In efficient bonding and poor adherence between paper and polyolefin film is particularly evidenced when the paper contain a filler or loading material. These fillers are frequently incorporated to increase the opacity of the paper, to provide a particular finish, to improve printing qualities, to increase the rigidity of the paper, etc. Some of the commonly used fillers are especially prepared clay, diatomaceous earth, chalk or calcium carbonate, gypsum or calcium sulfate, talc, and titanium dioxide.

Bonding and adhesion difficulties are also increased when certain sizing materials are used on the paper. Sizing is frequently used on paper to reduce surface fuzz and increase paper strength. Typical of some of the sizes used are starch and sodium silicate.

Polyolefin films and other articles commonly have a smooth and sleek, relatively slippery and wax like surface which is poorly adapted to provide for suitable adhesion or anchorage of applied materials by mere physical attachment. In addition, the relatively inert chemical nature of non-aromatic hydrocarbon polyolefins resist the efficient attachment of most materials by chemical inter-linkage or bonding.

Attempts have been made to bond polyolefins to non-regenerated cellulosic substrates employing various bonding agents, such as the melamine-formaldehyde resins, however, these methods have been generally unsatisfactory.

The present invention provides a process wherein paper, paperboard and analogous sheet-like substrates of non-regenerated cellulosic stock are effectively provided with a tightly adhered and firmly anchored coating or sheet-like layer of laminated non-aromatic hydrocarbon olefin polymer (including, as has been indicated, polyethylene, polypropylene, polybutylene, copolymers of ethylene and propylene, etc.) by a method which comprises initially applying to the surface of the paper substrate (or treating such surfaces with) a small quantity of a polyalkylene imine compound as an intermediate adhesion-promoting coat or layer; and subsequently applying over the polyalkylene imine treated surface of the paper substrate a fused or molten sheet-like coating layer of the desired polyolefin polymer; then cooling and solidifying the deposited polyolefin layer on the polyalkylene imine treated surface of the paper substrate.

The type of "paper" contemplated for use in the practice of the present invention is the commonly available paper, paperboard, and the like made from straw, bark, wood, cotton, flax, corn stalks, sugar cane bagasse, bamboo, hemp, and similar non-regenerated cellulose stock by such processes as the soda, sulfite or sulfate (Kraft) processes, the neutral sulfite cooking process, alkali-chlorine processes, nitric acid process, semi-chemical processes, etc.

The resulting composite or laminated film or foil structures or articles which may advantageously be obtained by practice of the present invention possess, to an unusual degree, practically all of the desirable and bene-

ficial attributes and properties of both the paper substrate layer and the applied polyolefin layer that are laminated therein. In addition, as indicated, the resulting composite structures are heat sealable in the conventional manner when joined under thermal welding conditions by means of the applied and laminated polyolefin layer. They are strong, tough and tear-resistant and have an attractive and highly decorative appearance. Their paper surface is more easily printable than plain non-aromatic hydrocarbon polymers. In addition, the laminated film product generally remains strong and flexible at relatively low temperatures and, of significance, is quite impermeable to most gases and vapors, being an effective moisture barrier.

Of paramount importance, as has been mentioned, the composite film product is capable of being strongly and efficiently heat sealed by joinder of the laminated polyolefin surfaces under the usual conditions in conventional thermal welding operations for plastic film.

The composite film or sheet-like products of the present invention are possessed of a strong and effective bond between the laminated paper and polyolefin layers. In most instances, the joined layers are extremely difficult, if not impossible, to strip apart or delaminate by ordinary physical methods.

The composite film and analogous sheet-like structures of the present invention have particular utility as wrapping and packaging materials for foodstuffs and for other articles such as pharmaceuticals, medicinal products, hardware, etc., especially in instances when it is desired to protect the packaged articles from unwanted change in moisture either by transfer of moisture into or out of the package. The film products are also advantageous for wrapping and packaging foodstuffs and other materials which are intended to be handled or maintained and stored at relatively low temperatures in a refrigerated, or even in a frozen, condition. Besides providing protection as a strong and tough flexible covering, they also more effectively prevent dehydration of the packaged articles and, where required, tend to avoid development of the condition known as "freezer burn" which frequently occurs in inadequately protected frozen foods. Other beneficial uses of the composite film structures are found in water resistant and waterproof building papers and in moisture barriers in insulating walls.

Although the advantageous composite articles resulting from practice of the present invention are herein predominantly illustrated and described as film, foil and similar sheet-like products that are particularly useful for bags and the like heat-sealable packages, it is readily apparent that in many instances other composite structures and articles may also be prepared and provided such as and including tubes, cartons, boxes and other containers, and liners therefor, and so forth.

Advantageously, the paper substrate film which is laminated with the applied polyolefin layer is a relatively thin film or sheet-like structure. Likewise, the laminated layer of the polyolefin resin that is bonded to the paper substrate by the intermediate polyalkylene imine adhesion-promoting coating on the surface of the paper substrate is a relatively thin deposit. In this way, there is provided an ultimate laminated film product of corresponding relatively little thickness. However, if the ultimate laminated product is to be used for cartons, boxes and the like, the paper substrate would advantageously be thicker, corresponding to that used in paperboard, pasteboard, etc.

Beneficial results, for examples, are readily obtainable when the substrate sheet has a thickness of about 1—5 mils when the composite films are used as wrapping materials. When the composite films are used in carton and boxes the substrate paper may have a thickness of 12—78 or more mils.

It is generally advantageous for the laminated polyolefin layer to have a thickness between about 1/4 mil and about 10 mils and may frequently be more advantageous for the thickness of the applied polyolefin layer to be between about 1 and 2 mils.

As mentioned before, the paper substrates that are contemplated as being adapted for employment in the practice of the present invention include any of the papers, paperboards, etc., made from non-regenerated cellulosic stock by any of the commercial paper-making processes, including papers that have been modified in certain respects, such as by the addition of certain fillers and sizing materials and printing inks.

The polyethylene or other non-aromatic hydrocarbon polyolefin which is employed in the practice of the present invention may be polymers of any normally solid and film-forming nature. For examples, the polymers of ethylene which are employed may be those, or similar to those, which sometimes are referred to as "polyethylenes" and which may be obtained by polymerizing ethylene in a basic aqueous medium and in the presence of polymerisation-favoring quantities of oxygen under relatively high pressures in excess of 500 or 1000 atmospheres at temperatures which may be between 150° and 275° C. Or, if desired, the ethylene and other non-aromatic hydrocarbon olefin polymers may be essentially linear and unbranched polymers, or polyolefin products similar to these materials. The essentially linear and unbranched, macromolecular, high density polyethylenes have been referred to as "ultrathenes". They ordinarily have greater apparent molecular weights (as may be determined from such characteristics

as their melt viscosities and the like) than the "polyethylene" type polyethylenes which are usually inexcess of 20000 and generally in excess of 40000; densities of about 0.94—0.96 grams per cubic centimeter; and melting points in the neighbourhood of 125—135° C. They are also ordinarily found to have a more crystalline nature than conventional polyethylenes and may contain less than 3.0 and even less than 0.3 methyl radicals per 100 methylene groups in the polymer molecule. The essentially linear and unbranched polymers of ethylene and other non-aromatic hydrocarbon olefins may be obtained under relatively low pressures of 1 to 100 atmospheres using such catalysts for polymerizing the ethylene or other olefin as mixtures of strong reducing agents and compounds of Group IV-B, V-B and VI-B metals of the Periodic System; chromium oxide on silicated alumina; hexavalent molybdenum compounds; and charcoal supported nickel-cobalt.

As is apparent, the polyolefin polymers utilized in the practice of the present invention are generally prepared by polymerization of monoolefinic aliphatic olefin monomers, such as ethylene, propylene, butylene and so forth (including polymerizable mixtures thereof) that contain from 2 to about 8 carbon atoms, which monomeric olefins are frequently known as being 1-olefins due to their characteristic terminally unsaturated structures.

The polyalkylene imines which are utilized for providing the intermediate adhesion promoting coating deposit in the composite film structures of the invention to secure the desired effective lamination between the paper and polyolefin layers are advantageously one of the polyethylene imines which are of the general structure: —

$$H—(—CH_2—CH_2—NH—CH_2—CH_2—NH—)_n—H$$

in which n has a numerical value of at least 1 and may be a larger, plural integer having a value as great as 1000—2000 and more. Thus, when a polyethylene imine is utilized for treating the surface of the substrate, it may be of any desired molecular weight in which the material can be obtained. It is generally most advantageous, however, to avoid use of very low molecular weight materials having excessive volatilities.

As is apparent, other polyalkylene imines equivalent to polyethylene imines (obtained by polymerization, in the known way, of the corresponding alkylene imines) may also be utilized as an intermediate adhesion-promoting coat to treat the surface of the substrate layer in place of, or in combination with, the polyethylene imine. Ordinarily it is of greatest practical significance for these to include any of the homologous polyalkylene imines which are comprised of alkylene units of less than about 4 carbon atoms. In most cases, although no limiting implications are intended, the polyalkylene imines of greatest interest to employ are the relatively low polymer, water-soluble materials whose viscosity in 20 percent aqueous solution at 20° C. are of the order of 100 poises.

Only a very small quantity of the polyalkylene imine need be deposited as an intermediate adhesive coating on the surface of the paper substrate to which the polyethylene or other non-aromatic hydrocarbon polymer layer is laminated. In general, an amount between about 5 grams and 100 grams per thousand square feet of substrate surface are suitable to facilitate and promote the adhesive of the polyolefin polymer layer on the substrate surface being laminated. Frequently, between about 20 and 50 grams per thousand square feet provides an entirely satisfactory result.

Although it can be directly applied if desired, the deposition of the polyalkylene imine is generally better and more conventionally and easily accomplished from a solution or dispersion of the adhesion-promoting agent in a suitable solvent, such as acetone, methyl ethyl ketone, methyl isopropyl ketone, lower alkyl alcohols (particularly those of less than 4 carbon atoms), etc. Methanol, ethanol and isopropanol are oftentimes found to provide optimum solvent behaviour for the polyalkylene imine. Advantageously, a relatively dilute solution of the polyalkylene imine treating agent in the solvent is employed, such as one having a concentration of the polyalkylene imine between about 1/8 and 1/2 percent by weight of the dissolved adhesion promoting agent. This facilitates the uniform and general deposition over the surface of the substrate of the relatively minute quantities of polyalkylene imine needed for the intermediate adhesion-promoting coating on the paper substrate prior to deposit or placement of the polyolefin polymer layer being laminated.

The deposition of the polyalkylene imine can also be applied from a water solution to the paper substrate with particular advantage since this application is readily adapted to paper mill practices.

When the polyalkylene imines (such as polyethylene imine) are employed in too great a concentration on the substrate surface, they tend to result in undesirably weak and unsatisfactory laminated structure.

The coating application of the polyalkylene imine anchor layer may be made by spraying or spread coating the solution thereof on the surface of the paper substrate being laminated to the polyolefin layer. Necessarily, the coating of the strongly cationic polyalkylene imine agent is dried by air or by means

of heat at an elevated temperature on the surface of the paper substrate prior to actual application thereover of the polyolefin layer being laminated therein.

In this connection, it is generally desirable to employ a relatively fugacious solvent in order to allow rapid and ready drying (with minimized or no external application of heat) of the applied polyalkylene imine solution. Thus, isopropanol, ethanol, or methanol are, as has been indicated, most beneficial to employ as solvents for the applicating solution of the polyalkylene imine. Such solvents can be easily dried in cool air (such as air at room temperature or with minimum requirements for heat) to deposit the adhesion promoting intermediate layer of the polyalkylene imine on the surface of the substrate. Frequently, however, the use of warm air is found to be more practical for drying, especially when conditions of relatively high humidity in the atmosphere are encountered.

It is generally advantageous to maintain the polyolefin in the extruder, particularly when it is polyethylene, at a temperature sufficiently high to ensure its remaining in a fused and molten condition after being passed from the die to fall through the air as a layer on the surface of the pretreated film. Thus, it is generally desirable for the extruded polymer to make contact with the pretreated substrate while it is at a temperature of at least 175°—190° C. (at actual contact or juncture with the pretreated substrate), particularly in the instances when polyethylene is being laminated. This generally requires the molten polymer in the extruder barrel, as it leaves the die lips, to be at a temperature between about 285° and 315° C.

Although the molten polyolefin may be passed any distance through the atmosphere from the outlet of the die to the point of juncture with the pretreated substrate, it is generally advantageous for a distance of not more than 30, advantageously about 15 to 25 cms to be utilized.

Immediately upon being applied, the polyolefin layer from the molten sheet is chilled, solidified and laminated in place by the action of a chill roll which is maintained at a temperature above the sticking temperature of the polyolefin but below its fusion point, which temperature, frequently, is most advantageously maintained in the range from about 26 to 37° C.

Great care should be taken in applying the molten polyolefin to the surface of the pretreated substrate. It is essential that the sheet of fused polymer to be laminated into the composite film product is not allowed to become solidified before contacting the treated substrate, as by first falling on the chill roll before entering the nip of the rolls wherein the lamination is effected. It is generally desirable to feed the molten polyolefin polymer on to the surface of the pretreated substrate just before the material to be laminated is passed through the nip of the cooperating rollers.

Actually, better results are generally obtained when the molten polyolefin makes initial contact or juncture with the substrate prior to being chilled at just about the nip of the rolls, although suitable results are obtained if contact is made some distance back before the nip. Generally, however, the actual lateral distance at which contact is made before entering the nip of the rolls should be within several centimetres and advantageously within about 2.5 cms from the nip of the roll.

In order to further illustrate the invention, a commercial grade of printing paper which had been heavily sized with starch was surface treated with polyethylene imine at the rate of about 3.78 liters of applicating solution per 13.6 kilograms of paper using an applicating solution consisting of about 1.5 per cent by weight, based on the weight of the applicating solution, of polyethylene imine in ethanol. This represented an actual application of about 15 grams of polyethylene imine per thousand square feet of paper surface. The polyethylene imine employed has an average molecular weight of about 7000.

The application of the polyethylene imine solution was made using gravure rolls having a diameter of about 15 cms and a width of about 1 meter for application of the solution to the paper substrate. After application of the polyethylene imine, the adhesion-promoting coating thereof was dried on the surface of the substrate in an oven at a temperature of about 65° C. prior to being taken up as a stock or supply roll of the intermediate pretreated substrate paper.

The thereby obtained pretreated substrate was then laminated with polyethylene. The polyethylene imine coated substrate paper was run at a linear rate of about 30 meters per minute under an extruder for the polyethylene discharging into the nip of a pair of rolls, consisting of a 45 cm diameter back-up roll and a 0.6 meter diameter chill roll (with the chill roll being maintained at about 26° C.), through which the substrate was being passed.

About a 2 mil layer of polyethylene was applied from the extruder to the pretreated substrate by feeding the molten polymer layer in the form of a falling sheet or curtain (through about a 20 cm fall) from the die lips to the nip of the rolls. The temperature of the polyethylene in the barrel of the extruder at the die was about 315° C. Its temperature at contact with the substrate was about 190° C.

The polyethylene employed was the conventional, branch-structured variety of polyethylene (of the "polythene type) having a

melt index (according to ASTM D-1238-52T) of about 3.0. After being cooled and solidified and laminated in place, the resulting composite film structure was taken up into a supply roll.

The laminated layers of the composite film structure were exceptionally well bonded together and could not be separated without causing fiber tear in the paper layer.

In contrast, when the same starch-sized printing paper was treated the same as above, excepting to eliminate the application of the polyethylene imine, no adhesive bond was formed between the paper and polyethylene layers.

Excellent results are obtained when the foregoing procedure is repeated using other papers. Papers, paperboards, and the like which have incorporated in or on them other sizes and/or fillers, etc., or which have been printed upon prior to the application of the polyethylene imine give good results. Of course, raw paper, or paper that is absent any fillers, sizes, and the like or otherwise unmodified is highly suitable and gives excellent results.

About the same results are obtained when the foregoing procedure is repeated excepting to laminate essentially linear and unbranched polyethylene in the composite film structure being made; or to apply a layer of polyethylene or a layer of a copolymer of propylene and ethylene (such as one containing about equal weight percentages of each monomer in the polyolefin product) on the treated substrate, or when other polyalkylene imines within the scope indicated in the foregoing specification are employed to provide the adhesion-promoting coating on the surface of the substrate with which the polyolefin layer is laminated.

WHAT WE CLAIM IS:—

1. Process for the production of laminate structures and particularly of laminated films or foils and the like, which consist of or contain a non-regenerated cellulosic substrate to at least one side of which is intimately joined a layer of a non-aromatic hydrocarbon polymer, such as polyethylene or polypropylene, which comprises applying a polyalkylene imine to at least one surface of the cellulosic substrate, and thereafter depositing a non-aromatic hydrocarbon polymer in the form of a molten polymer layer over the intermediate coating of the polyalkylene imine.

2. Process as claimed in Claim 1, wherein the polyalkylene imine is applied to the surface of the substrate in a volatile solvent such as water or a lower alkyl alcohol, and the solvent is removed from the substrate by drying.

3. Process as claimed in Claims 1 or 2, wherein the substrate contains a non-resinous size and/or an inorganic filler.

4. Process as claimed in any one of Claims 1 to 3, wherein the cellulosic substrate is printed upon before the application of the polyalkylene imine.

5. Process as claimed in any one of Claims 1 to 4, wherein the polyalkylene imine is applied to the surface of the substrate in an amount between 15 and 50 grams per thousand square feet of substrate surface.

6. Process as claimed in any one of Claims 1 to 5, wherein the polyolefin layer is placed in contact with the polyalkylene imine treated substrate at a temperature of at least 175°—190° C., but below the decomposition temperature of the polyolefin.

7. Process as claimed in any one of Claims 1 to 6, wherein the polyalkylene imine has 2 to 4 carbon atoms in the alkylene units.

8. Process as claimed in Claim 7, wherein the polyalkylene imine is polyethylene imine.

9. Laminate structure which consists of a non-regenerated cellulosic substrate intimately joined and tightly adhering to a polyolefin film by means of an intermediate adhesion promoting layer of a polyalkylene imine.

10. Laminate as claimed in Claim 9, wherein the polyalkylene imine has 2 to 4 carbon atoms in the alkylene units.

11. Laminate as claimed in Claim 10, wherein the polyalkylene imine is polyethylene imine.

12. Laminate as claimed in any one of Claims 9 to 11, wherein the substrate contains an inorganic filler, and/or a non-resinous size and/or a printing ink.

13. Laminate as claimed in any one of Claims 9 to 12, wherein the substrate layer is coated with between 15 and 50 grams of the polyalkylene imine per thousand square feet of substrate surface.

14. Laminate as claimed in any one of Claims 9 to 13, wherein the polyolefin is polyethylene or polypropylene.

15. Process for the production of laminate structures substantially as hereinbefore described with reference to the specific examples.

16. Laminate structures whenever prepared by the process claimed in Claim 15.

BOULT, WADE & TENNANT,
111 & 112, Hatton Garden, London, E.C.1,
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Agents for the Applicants.

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